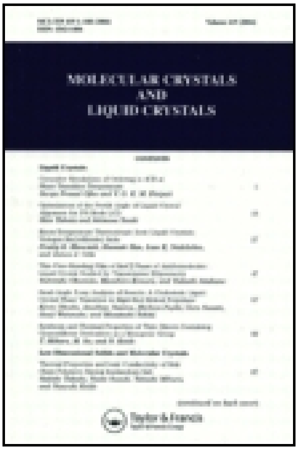

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ON THE RELEVANCE OF CERTAIN TRANSPORT-STRUCTURE CORRELATIONS IN $SBCL_5$-INTERCALATED GRAPHITE TO OUR OVERALL UNDERSTANDING OF GIC c AXIS CONDUCTIVITY

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Abstract This paper presents some new data on the $SbCl_5$-intercalated graphite family as concerns the relationships between c axis resistivity, $\rho_c(T,p)$,and intercalate layer structure. Results on the influence of intercalate layer crystallization and the nature of the host graphite are discussed and compared with those on other GIC families. Certain data are examined in the light of available theories and such an analysis raises a number of questions.

INTRODUCTION

Over the past several years, we have carried out a number of studies on the c axis electrical transport and the structural characterization of $SbCl_5$ intercalated highly oriented pyrographite (HOPG) and single crystal (SC) graphite[1-4]. These studies aimed at correlating the effects of temperature (T = 4.2 - 295 K) and applied pressure (p = 0 - 0.8 GPa) with the states of crystallization of the intercalate layer and the observed conductivity particularly in the c direction, $\sigma_c = 1/\rho_c$.

In this paper we will specifically treat only a limited number of results on the $SbCl_5$ family of GICs, these being chosen because they appear relevant to a larger class of GICs. We have selected two principal themes: the nature of the host graphite and the role of the intercalate layer. We will present a number of observations concerning these features drawn from our own experimental work and based on insight furnished by the ensemble of results in this field. One aim of this paper is also to raise the questions posed by the experimental results when one tries to interpret them in the light of current theories.

EXPERIMENTAL

Synthesis conditions for the $SbCl_5$ GIC's are given in detail elsewhere[1-4] and appropriate references to other GICs will be indicated below. It will suffice here to note that in as many cases as possible, our transport and X-ray studies were done on the same samples.

RESULTS AND DISCUSSION

Let us summarize briefly the results of our $\rho_c(T,p)$ studies on the $SbCl_5$ GICs:

- SC-based samples are generally better conductors than HOPG-based samples whatever the stage as illustrated in figure 1.

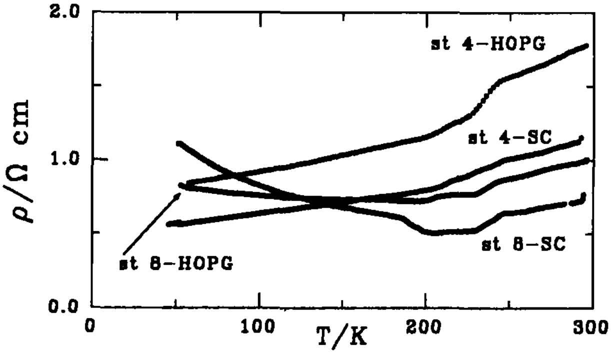

Fig. 1 c axis resistivity for stage 4 and 8 $SbCl_5$ GICs. In both cases, top samples are HOPG-based, bottom ones are SC-based.

- Crystallization within the intercalate layer whether due to lowering of T or application of p, always leads to lower ρ_c than when in the liquid state
- Different states of crystallization give rise to different values of ρ_c : the values are reproducible upon T cycling.
- The sign of the temperature coefficient of ρ_c (TCR) is stage-dependent but independent of the state of the intercalate
- Whatever the sign of the TCR, applying pressure always decreases $\rho_c(T)$.

Let us now examine the possible generalizations of these features to other GICs. As regards the enhanced c axis conductivity of SC- versus HOPG-based samples, this has also been observed in our studies on graphite intercalated with $HClO_4$[5] and $M_xAl_2Cl_8$ (M = Cu, Pd)[6]. This is an intriguing point since $\rho_c(T)$ is semiconductor-like in HOPG and both "metallic" and two orders of magnitude smaller in SC graphite. Intercalation thus results in a layered material in which the host appears to play a relatively minor role in determining the absolute value of resistivity and the final compound has almost completely "lost its memory" of whether the host was HOPG or SC. We should underline that while the host is a true SC, intercalation into a SC does NOT lead to a SC, exept in rare cases[6]. We conclude that "something" intrinsic to SC samples remains after intercalation which leads to greater σ_c and this appears to be a stage independent feature. The only exception we know is the lower T portion of the 8th stage sample of figure 1.

Crystallization, whether T- or p-provoked always gives rise to better c axis conductivity. This has also been observed in other GICs for which the liquid state is the RT state but for which the layer can crystallize as T is reduced. Indeed, this has also been noted in other $SbCl_5$ studies[7] and in GICs such as those containing AsF_5[8] and HNO_3[9].

Different crystallized states give rise to different values of resistivity. This was shown to be remarkably true in the case of an SC-based 8th stage $SbCl_5$ sample which underwent a series of different states of crystallization over a relatively limited range of temperature, as shown in figure 2. While in this case, the SC nature of the host allowed directly correlating in-plane unit cells and $\rho_c(T)$, discerning the underlying reason for the correlation is less straightforward: are different values in ρ_c to be attributed to the contributions of the different states of crystallization or to effects associated with the different quantities or natures of the uncrystallized state or to locally different stacking arrangements?

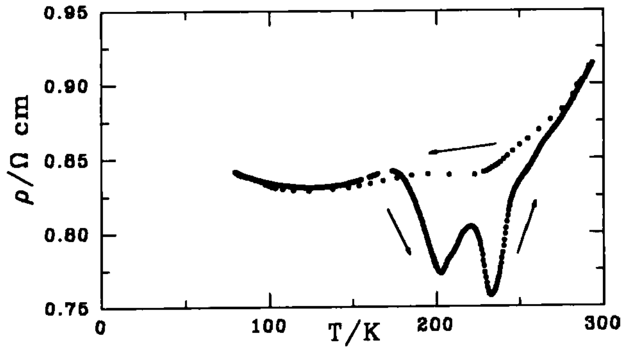

Fig. 2 $\rho_c(T)$ for 8th stage compound. Minima and maxima correspond to different states of crystallization of intercalate layer.

The TCR is stage dependent. This has been observed almost since the very first studies on K compounds[10]. We also underlined this is a review of experimental results[11] and was clearly shown in several works treating a range of stages in acceptor GICs, notably $FeCl_3$[12], $SbCl_5$[1-4,7] and donor compounds such as those containing an alkali metal and bismuth[13]. Our $SbCl_5$ study also revealed that it was independent of the state of the intercalate. Compounds which were quenched (stage 8) possessed a same negative TCR as slowly cooled crystallized or pressure crystallized samples. Similarly, rapidly cooled rich samples with a positive TCR also manifested a positive TCR upon slow cooling through the crystallized state which provoked a dramatic change in ρ_c. Finally, related to this last point, the TCR is independent of the absolute value of ρ_c, contrary to the Mooij-type relationship often found in other conducting materials[14].

Independent of the TCR, applying pressure provokes an increase in conductivity. This is independent of the p-initiated crystallization and is also observed in GICs containing HNO_3[15].

What questions do the above statements raise in the light of the numerous theories which have been proposed to date? Explaining c axis transport in intercalated graphite has proved to be a more complex task than in the host materials and even today making any kind of quantitative prediction about the absolute value or the thermal variation of ρ_c to be expected for a given GIC of defined intercalate, stage, etc. has not been done. The proposed mechanisms include anisotropic band conduction[12,16] variable range hopping[12], impurity-assisted (IA) and phonon-assisted (PA) hopping[17,18], interlayer conducting paths (CPs)[19], carrier interactions with LO phonons[19], and the presence of stacking faults[17,18] and small polarons[18]. Aside from the anisotropic band possibilities[16] for which only fixed T calculations were made, other works all require at least two mechanisms, and in many cases, far more. In the most recent and complete treatment of Sugihara[18], what can be concluded is the following. The lowest stage materials should have a "metallic" variation of $\rho_c(T)$ primarily due to interlayer charge transfer through "impurities" and CPs with essentially constant ρ_c at low T. For the higher stage materials, the negative $d\rho_c/dT$ requires the addition of an activation process across stacking faults and/or Daumas-Hérold (DH) boundaries.

The fact that both crystallization and pressure always lead to increased σ_c - whatever the TCR and stage - leads to believing that some small number of mechanism is dominant for all compounds, both rich and poor (up to say tenth stage). Might this not also be supported by the intercalate-state-independence of the sign of the TCR? i.e., the state influences the density of CPs, "impurities" or associated potential wells, but does not change the type of mechanism Perhaps, as in polymers, one mechanism can explain sign and another the magnitude?

Indeed, with the conducting polymers, the macroscopic measured conductivity is the sum of an intrinsic intramolecular contribution as well as intermolecular, interdomain and interfibrillar processes. It was demonstrated by Kaiser and Graham[20] that the conductivity of the conducting polymer could retain the T-dependence of the barrier regions but be "amplified" by geometric factors depending on the relative lengths of the highly conducting regions.

We must not forget that the conductivity integrates all types of defects within its framework. We recall that the behaviour of $\rho_c(T)$ in SC graphite is sometimes taken as being the intrinsic behaviour and in HOPG this is strongly modified by stacking faults responsible for both the higher resistivity and the negative TCR. Similarly, in GICs, in addition to the low stage conductivity processes, Sugihara explained the higher resistivity and different TCR in higher stage GICs by other terms accounting for activation across stacking fault planes and/or DH walls[17,18]. In a given GIC, among the "defects" are:the following. There are stacking faults within a given crystallographically-defined domain. We recall that c axis correlation length is very limited even in the best of cases. A given domain may be side-by-side other domains of different unit cells, or intermingled with amorphous or disordered regions, the ensemble being (perhaps) within a DH domain. Finally, the domains themselves may be separated by other barriers, probably necessitating an activation energy

One point that appears to remain unclear as regards the crystallization and its effect on $\rho_c(T)$ is to what aspect one should attribute the enhanced conductivity. It might be possible to attribute the different values (e.g., fig. 2) to different amounts of crystallized area, to the different crystallization types or to different quantities of uncrystllized region. The theories of Sugihara[17,18] explain the c axis conductivity in low stage GICs by IA hopping or CPs. so what is the meaning of attributing more "impurities" to crystallized than to amorphous or liquid regions? In the same line of thought, the SC versus HOPG question would lead to concluding that intercalated SCs have more CPs or IA centres than does intercalated HOPG. Furthermore, we would also expect that CPs would be "frozen in" at low T - but at low T, the lowest $\rho_c(T)$ - the highest $\sigma_c(T)$ - values are for stage 1 GICs almost without exception. So, what would the CPs be physically?

The concept of several parallel mechanisms also raises some questions. For instance, we know that the in-plane mobility is high so that if mechanisms operate in parallel, we would expect electrons to "choose the path of least resistance". Why does $\rho_c(T)$ rise upon intercalation? Even for a relatively poor, but "true" GIC ρ_c is greater than in the host. Since there are many side by side graphite layers; say five to ten, we might expect that correlation would exist over this length, so that locally we would have a graphite SC. But would one not then expect the high in-plane mobility to "allow" the carriers to seek the lowest resistivity paths?

CONCLUSIONS

The c axis transport properties of GICs are very rich and numerous open questions remain. Ubbelohde, a pioneer in the field of GIC chemistry and characterization wrote over two decades ago: "Conduction mechanisms across the layers may be complex and further discussion must await data ... down to 4K and below, as well as measurements at enhanced pressures which compress the sandwiches and modify the charge transfer."[21] While both of these objectives have been met, his comment made four years later remains remarkably true today: "Particularly in the direction of the c axis ...there are likely to be some interesting surprises ahead"[22]. Future study should perhaps aim at simpler systems so as to untangle some of the complex interrelationships governing c axis conductivity.

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